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OUTGASSING MEASUREMENTS OF A THERMAL BLANKET AND A SPACE CHAMBER USING QUARTZ CRYSTAL MICROBALANCES

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ABSTRACT

The outgassing characteristics of an ERTS-type thermal blanket used as an insulation shell for the attitude control system of a spacecraft were investigated. A test conducted in a vacuum chamber established the thermal blanket's outgassing rate, the nature and mechanism of the outgassing, and determined its rate of deposition on surfaces at different temperatures. The test established a method for measuring outgassing and the temperature and the duration for such outgassing. For about 60 hours the blanket was degassed. The measurements of the quantities and the identification of the material were obtained as follows: (1) accretions on quartz crystal microbalances (QCM) held at -120 and -10°C ; (2) mass spectrometer analyses of the gases in the chamber; (3) analysis of the condensates on a cold finger at -196°C by infrared spectroscopy and gas-chromatography/mass-spectrometry; (4) identification of the vapor pressures of the accreted materials by temperature cycling of the QCMs. In 60 hours, the blanket outgassed a total of about 0.1 g of material that included hydrocarbon oxides, phthalates and tetrabutoxyethylene. One tenth of this material appeared to have vapor pressures varying from 2×10^{-8} torr at -50°C to 3×10^{-7} torr at -1°C . The surface at -10°C collected about $7.5 \times 10^{-6}\text{ g/cm}^2$ of this material during the duration of the test.

INTRODUCTION

The vacuum chamber test described had as its overall objective the study of the outgassing of an ERTS thermal blanket. The removal or reduction of outgassing from the blanket is important because the outgassed products can condense or be adsorbed on critical surfaces of the spacecraft. When this occurs, the optical and thermal properties of these surfaces can degrade.

More specifically, the objectives of this study were to determine the quantity of outgassed material, its accretion rate at various surface temperatures, its chemical nature, and its outgassing mechanisms. Implicit in the test was the development of the method of measuring the outgassing, the temperatures to be used, the duration of the test, the instrumentation, and the instrument locations.

BLANKET AND TEST FACILITY DESCRIPTION

The ERTS-type blanket consisted of about 30 layers of mylar that were crinkled and aluminized on both sides (polyethylene terephthalate and 99 percent pure aluminum) and sandwiched by supports consisting of glass cloth and Epon 815 (on epoxy catalized by triethylene tetramine). These supports were painted with D-4D alkyd silicone paint and held together with nylon thread and polyamide buttons. The blanket's generally trapezoidal shape had a surface estimated at about 8500 cm² on each side.

For the test, the blanket was suspended vertically inside the Test and Evaluation Facility No. 240 vacuum chamber. This chamber has a nominal working volume of 0.6 m³. It is pumped by a 66-1/s mechanical pump and by a 5300-1/s diffusion pump. Provisions for heating to 100°C and cooling to liquid nitrogen (LN₂) temperature of the Cat-A-Lac flat, black, painted shroud are provided. The pressure measurements are made with alphasatron and ion gages. Measurements of pressure and temperature are transmitted to a central data collection station on 12 channels at 100-s intervals. An LN₂ cooled "finger" is used to collect condensable materials. The pumping speed of the chamber under molecular flow conditions is approximately 1000 l/s.

OUTGASSING, MASS DEPOSITION, AND MASS SPECTRA ANALYSIS INSTRUMENTATION

Two quartz crystal microbalances (QCMs), a quadrupole mass spectrometer, and an LN₂ cooled finger comprised the instrumentation. Of the two microbalances, one was operated at -120°C and measured the total outgassing. The other was operated at -10°C, a slightly lower temperature than sensitive spacecraft surfaces would experience in orbit, hence a conservative indication of contamination. The LN₂ cold finger provided a cumulative record of the condensable outgassing for the duration of the test. Washings from the cold finger provided the material for infrared radiometry and gas chromatographic/mass spectrometer analysis of the condensate. The quadrupole mass analyzer was suspended in the chamber in the same region as the microbalances and provided real-time analyses.

QUARTZ CRYSTAL MICROBALANCES

The microbalances consisted of two piezoelectric quartz crystals of the same cut and dimensions. They were matched to have the same resonant frequency and same temperature response. The two crystals of the unit, maintained at the same temperature, were excited by electric charges to vibrate at resonance during operation. When one of the crystals was shielded from the gas flux while the other crystal accreted

mass, a beat frequency was established between the two. The beat frequency Δf is related to the mass accretion Δm by the relation¹

$$\Delta f = - f_0 \frac{\Delta m}{\rho t A} = - c_f \frac{\Delta m}{A} \quad (\text{Hz}) \quad (1)$$

The crystals used in these tests had an f_0 of 10^7 Hz, a thickness $t = 1.7 \times 10^{-2}$ cm, an area $A = 0.2 \text{ cm}^2$, and a density $\rho = 2.65 \text{ g/cm}^3$. Therefore, their sensitivity factor c_f , was $2.22 \times 10^8 \text{ Hz cm}^2 \text{ g}^{-1}$. Deviation from the linear relation would occur when Δf becomes too large. In the tests, Δf was never allowed to exceed 10^5 Hz so that the deviation was always less than

$$D = \frac{2 \Delta f f_0}{f_0^2} = 2\%$$

This was accomplished by warming the QCM and therefore unloading the crystal when the Δf reached a value of approximately 70 to 80×10^3 Hz. After unloading, the crystal was returned to -120° C , and the accumulation continued.

The conductance of the port leading to the vibrating surface of the crystal operating at -120° C was calculated to be 1.86 l/s for air at 25° C . The other crystal unit operating at -10° C had focusing lenses at the entrance. Its conductance for the same gas conditions was 1.13 l/s.

TEST PROCEDURES

The chamber was evacuated to a pressure of 10^{-5} torr or lower, while the chamber walls and the blanket were held at the ambient temperature. The customary pumping procedures were followed. At this pressure, the temperatures of the shroud and blanket were raised to $+60^\circ \text{ C}$, refrigerant was admitted to the -10° C crystal, and LN_2 was directed to the -120° C microbalance and the cold finger. A rapid rate of mass accretion (due mostly to water) was normally noted and it became necessary to unload the crystal within a relatively short period. This prevented the deviation from linearity of the mass-frequency relation of the crystal or the complete loss of oscillation. This unloading, however, became less frequent as the condensable gases in the chamber were depleted and the outgassing was reduced. The unloading was accomplished in a manner that allowed the retention of a certain amount of condensed mass on the crystal. Previous tests had established that, upon unloading the crystal, a rapid drop of frequency would be followed by a slow drop. This indicated that a material or materials with a low vapor pressure at the temperature of crystal unloading had been accreted together with more volatile materials. Accordingly, in these

tests the unloading was accomplished by increasing the temperature to -55°C from -120°C . At this temperature, the vapor pressure of water is about 10^{-2} torr, and, in an environment where the partial pressure of water was at least two orders of magnitude lower than 10^{-2} , the water on the crystal evaporated within a short period of time. The time at which this evaporation was accomplished was obvious from the frequency rate of change. When evaporation of the volatile material was complete, the frequency changed slowly. In the warming periods of these tests, an increase in pressure in the chamber resulted from the release of condensed gases on piping and other surfaces of the QCM. The normal accretion on the crystal was resumed by cooling the crystal to the test temperature of -120°C . This cycle lasted from 15 to 20 minutes during which time outgassing from materials continued, but the recorded data were complicated by the fact that crystal temperature effects obscured mass information. However, the accretion which would have occurred during these unloading periods was estimated by matching the slopes of the frequency curve before and after the crystal unloading.

THE QCM MEASUREMENT OF OUTGASSING

The crystal microbalance at -120°C registered the accumulation of molecules that impinged and remained on the sensing surface. This amount, however, was less than the total quantity emitted by the blanket and chamber because most of the gases were removed by the chamber pumping system and by other cold surfaces in the chamber. Further, the QCM had a conductance limiting passage to the crystal. The mass balance can be expressed as throughput. Restating the above,

$$Q = Q_p + Q_1 + Q_2 = (S_p + S_1 + S_2) P$$

where Q_p and S_p are the throughput and speed of the pumping system and cold surfaces in the chamber other than the QCM; Q_1 and S_1 are the throughput and pumping speed of the -120°C microbalance unit; Q_2 and S_2 are those of the -10°C microbalance in the chamber; and P is the isotropic pressure in the chamber. The values of the pumping speeds have already been indicated: $S_p = 1000$ l/s, $S_1 = 1.86$, and $S_2 = 1.13$ l/s. The pressure P can be obtained in terms of the throughput at the surface of the -120°C crystal, as $P = S_x P_x / S_1$ where P_x and S_x are the pressure and surface speed at the crystal. Inserting these values in the mass balance equation, changing to mass, and noting that the mass on the crystal as shown in Equation 1, is

$$\Delta m = \rho S_x P_x dt = \frac{\Delta f A}{C_f}$$

one obtains

$$W = \rho \int Q dt = \left(\frac{S_p + S_1 + S_2}{S_1} \right) \rho S_x P_x dt = (536) \frac{\Delta f A}{C_f}$$

$$= 4.82 \times 10^{-7} \Delta f \quad (g) \quad (2)$$

where $S_p + S_1 + S_2/S_1 = 536$, the constant that accounts for the unit restriction and for other pumping systems in the chamber. The total outgassing of condensables on a -120°C surface, expressed in grams, is therefore the change in frequency of the -120°C crystal times the constant (536).

THE QCM MEASUREMENT OF ACCRETION ON -10°C SURFACE

The -10°C unit had been designed for measurements of beaming effects and had been provided with focusing lenses. The mass registered by this unit was therefore less than it would have been with an unrestricted passage. To account for this lower mass, one can reason as follows. The pumping speed of the crystal microbalance passage leading to the vibrating crystal was calculated to be $S_2 = 1.13 \text{ l/s}$ for air at 25°C . The crystal pumping speed² was $S_x = 11.6 \times 0.2 \text{ l/s}$ for a 0.2 cm^2 area and for the same gas conditions. The correction factor to be applied to this unit to account for the flow restriction was then $S_x/S_2 = 2.05$. The mass W , which would be registered by the unobstructed unit, is

$$W = (\rho S_x P_x dt) \frac{S_x}{S_2} = 2.05 \frac{A \Delta f}{C_f} = 1.84 \times 10^{-9} \Delta f \quad (g) \quad (3)$$

The mass per unit area is

$$\frac{W}{A} = \frac{1.84 \times 10^{-9}}{0.2} \Delta f = 9.23 \times 10^{-9} \Delta f \quad (g/\text{cm}^2) \quad (4)$$

The above relationships do not account for the effect of the chamber pumping speed, and, this QCM measured the accretion corresponding to the actual gas conditions in the chamber.

OUTGASSING OF THE 3- BY 3-FOOT CHAMBER

In advance of the degassing of the blanket, measurements of the empty chamber outgassing were carried out. The chamber was evacuated to a pressure of about 10^{-7} torr, and its walls were held at $+60^\circ \text{C}$. Following the procedure described above, the two microbalances were brought to -10°C and -120°C . No accretion was

measured throughout the test on -10°C . The -120°C unit required unloading several times to prevent excessive accretion. However, the unloadings to -55°C temperatures and return to -120°C were performed mainly to establish the amount of low vapor pressure materials on the crystal. The test was carried out for about 26 hours. It was terminated when it appeared that the rate of accretion on the crystal was minimal. The accretion expressed as mass versus time, due to chamber outgassing, is shown in Figures 1 and 2. Figure 1 shows the total accumulation on the crystal and Figure 2 shows the amount of the total that did not evaporate rapidly at -55°C . The amount in grams is obtained as the product of the frequency and the constant derived previously. For a 24 hour outgassing, these were $7.5 \times 10^{-2}\text{ g}$ total outgassing of which $1.68 \times 10^{-3}\text{ g}$ are of the heavy molecular weight material. The rates of degassing as a function of time are shown in Figure 3. These rates were obtained from Figures 1 and 2, and they reveal considerable information about the chamber outgassing. The slope of the total degassing is -1 . This is representative of the simultaneous surface desorption of several materials when each has a different heat of desorption³. The low vapor pressure material outgassing showed an initial slope of about $-1/2$ for the first 6 or 7 hours followed by what appears to be a -1 slope. The initial slope is characteristic of processes of a diffusional nature. Therefore, this material consisted mostly of molecules of diffusional origin for the first 6 or 7 hours and then mostly of molecules from surface desorption. After several hours the surface desorption is still present, and this could imply that the material of desorption origin was tightly bound to the surface such as in a chemisorbed state. On the other hand, the surface desorption was the predominant outgassing, as shown by the total rate curve. The curve plots show that the total outgassing decreased from an initial $4 \times 10^{-6}\text{ g/s}$ to an order of magnitude lower in about 10 hours. In 100 hours of pumping, the magnitude would be another decade lower. The low vapor pressure material outgassing rate was initially about $1/10$ of the total, that is, approximately $5.5 \times 10^{-8}\text{ g/s}$. It became about $1/2$ of the total rate after about 10 hours. In about 35 hours of pumping, its magnitude was about $1/10$ of the initial rate (or about $1/100$ of the total rate). These times are predicated on $+60^{\circ}\text{C}$ surfaces. An estimate of corresponding times for other outgassing temperatures is given later. In regard to the nature of the gases, the periodic mass spectrometric analyses and the cold finger analysis at the end of the test indicated that the gas was mostly water with traces of phthalates and hydrocarbons.

BLANKET OUTGASSING

Mass accretions on the -120°C microbalance due to blanket outgassing are also shown in Figures 1 and 2. Figure 1 pertains to total outgassing and Figure 2 to the portion of the total outgassing that consisted of materials having a lower vapor pressure at -55°C . The net accretion due to the blanket (obtained by subtracting the results of the empty chamber test from those including the blanket) are shown in these figures. Figure 1 shows that the blanket lost material at a rapid rate during the initial hours of the test. The rate decreased steadily after that, and when between 24 and 36 hours, it appeared to become constant. A tendency toward a decrease in rate appeared to develop after 56 hours of degassing. However, this is not apparent from the curve and could not be established with certainty because data from the empty chamber was not available for times beyond 26 hours. The plots in Figure 2 show the material, originating from the blanket and chamber, that remained on the crystal when it was brought to a temperature of -55°C . The relative magnitude and slopes of the curve with respect to that found for the empty chamber indicate that the material was definitively of blanket origin.

For convenience, Table 1 indicates the cumulative losses at discrete times.

Table 1
Blanket Weight Loss

| Time (hr) | Total Weight Loss (g) | Material Loss with Low Vapor Pressure at -55°C (g) |
|--------------|----------------------------|--|
| 12 | 6.07×10^{-2} | 6.15×10^{-3} |
| 24 | 7.61×10^{-2} | 7.76×10^{-3} |
| 36 | 8.58×10^{-2} | 8.77×10^{-3} |
| 48 | 9.44×10^{-2} | 9.56×10^{-3} |
| 60 | $\sim 1.05 \times 10^{-1}$ | $\sim 1.03 \times 10^{-2}$ |

As shown, most of the material losses occurred during the first 12 hours of degassing. Additional losses after this time were of diminishing magnitudes.

The outgassing rates are shown as a function of time in Figure 4. The rates decreased an order of magnitude in about 15 hours. Thirty to 40 hours after initial degassing, the rate became almost constant, with a value of about $2.5 \times 10^{-7}\text{g/s}$. The total outgassing rate appeared

to approach an inverse proportionality to the square root of the time. This is characteristic of diffusion processes. The deviation from this process may be due to the inclusion of surface desorption. The constant rate approached at the end of 30 to 40 hours could have been caused by material sublimation or by a constant leak such as one which could be produced by the slow venting of the volumes between mylar layers. On the other hand, the low vapor pressure material rate appeared to follow a diffusional process ($t^{-1/2}$) during the first 6 or 7 hours, followed by a t^{-1} process that is characteristic of surface desorption of a combination of several materials. The outgassing rate of heavy materials became constant with a value of about 1.8×10^{-8} g/s at about the same time that the total outgassing approached a constant. The conclusions for long term degassing should be moderated by the fact that data for the empty chamber after 26 hours were extrapolated.

The plots of Figures 1 and 2 are typical of the weight loss curves obtained from the outgassing of organic materials. Outgassing during the initial hours typically consists of physically adsorbed gases, evaporation of certain additives and unreacted fragments, and the evaporation of low molecular weight components of the material itself. The physically adsorbed gases consist mainly of water. Additives and fragments, consisting of stabilizers, plasticizers, solvents, and unreacted varieties, diffuse to the surface before their evaporation takes place. The evaporation of the material will consist of the loss of all its molecular components.

During the described testing the outgassing curve of the blanket included a certain amount of gas trapped between the layers of mylar. This outgassing should occur at a constant rate for a short period of time. The combination of all these outgassing mechanisms would appear as has been shown by the test, that is, an exponential curve followed by a quasi-constant rate weight loss.

DEPOSITION OF BLANKET OUTGASSED MATERIAL ON -10°C SURFACES

The outgassed material that accumulated on a -10°C surface as provided by the microbalance, is shown in Figure 5. This temperature was chosen to represent the lowest temperature that could exist at some critical surface of the spacecraft while in orbit. The temperature chosen was conservative because the spacecraft should not experience temperatures lower than -4°C . The figure does not show accumulation for the empty chamber test because the crystal did not show changes accountable to mass accretion during that test. The curve shows that one half of the total deposit occurred within the first 2 hours of the test. In contrast, Figure 1 shows that one-third of the total outgassing occurred during the same period. The accretion on the surface of the crystal held at -10°C was 6.25×10^{-6} g/cm² after 24 hours and about

$7.6 \times 10^{-6} \text{g/cm}^2$ after 60 hours.

The rate of accretion on a unit surface is shown in Figure 6. The rate decayed more rapidly after 10 to 12 hours and became less than $1 \times 10^{-11} \text{g/cm}^2 \cdot \text{s}$ after 30 hours. It should be understood that the accretions obtained here are predicated on the conditions existing in the chamber and would not be the same under other conditions. An external surface of the spacecraft in orbit at -10°C could be exposed to lower partial pressures of the contaminating gases and accretion might not occur. On the other hand, a surface at this temperature in an enclosure or exposed directly to the same flux would accrete this amount for the duration of the outgassing. In regard to the material accreted on the crystal, one can consider the following. The saturated vapor pressure of water at -10°C is a few torr. Water vapor condensation on this surface could not occur unless its partial pressure was quite high, that is, greater than the saturated vapor pressure. The accretion must be attributed to materials with low saturated vapor pressure at -10°C . The accretion in 12 hours corresponding to $5.25 \times 10^{-6} \text{g}$ could consist of about 20 monolayer for a material assumed to have a molecular weight of 300 grams. The quantities of the materials accreted during the entire test were small, and a determination of the nature of the material or materials was impossible on the actual microbalance sensing surface.

EFFECT OF TEMPERATURE ON OUTGASSING RATES

A crude estimate of the effect of temperature on the rate of outgassing, and the time to accomplish a certain degree of degassing of the blanket or chamber can be obtained as follows. If one assumes that the degassing proceeds according to a first order reaction rate law, then the time for degassing is $t = Ke^{A/T}$ for a temperature T , where K and A are constants for the reaction⁴. Therefore, assuming that the process of degassing in the present test was completed in 24 hours with a temperature of 60°C , the time to obtain the same condition at other temperatures would be roughly as follows:

| | | | | |
|-----------------|-----|-----|-----|------|
| Temperature (C) | 20° | 60° | 80° | 100° |
| Time (hrs) | 37 | 24 | 20 | 17 |

This indicates that at the ambient temperature of 20°C , the degree of degassing accomplished in this test, would be obtained in 37 hours rather than in 24 hours.

IDENTIFICATION OF OUTGASSED MATERIALS

Throughout the tests, the chamber gases were monitored with a quadrupole mass analyzer and by a cold finger that provided samples for infrared spectrometry and gas chromatography/mass spectrometry analysis.

The residual gas analyzer provided an identification of the blanket contributed molecules by comparing scans made during the empty chamber test and the test including the blanket. Three peaks at $m/e = 77$, 105, and 122 stood out as blanket contributed molecules. These are shown as a function of time in Figure 7. These fragments per se are insufficient to identify the materials. Further considerations indicated that they are probably hydrocarbon oxides. No amines were present, which eliminated nylon and glass cloth as contaminants.

Gas chromatography/mass spectrometry identified phthalates and tetrabutoxyethylene. The phthalates are so commonly found in these tests as to be practically omnipresent. The tetrabutoxyethylene is often used to cause paint to flow and may have originated from the D-4D paint used on the blanket. In conclusion, it is difficult to ascribe these molecules to particular materials from the conditions found in these tests. It can be stated, however, that most peak heights are decreased by at least one decade within the first 24 hours of pumping. Total decreases after 72 hours rarely exceed two decades without any indication that further decreases would result beyond that time. This behavior is also shown in Figure 7.

At the conclusion of the test period, an attempt was made to obtain vapor pressure data for the materials deposited on the -120°C microbalance. The microbalance showed that a sublimation rate of $1 \times 10^{-9} \text{ g/cm}^2/\text{s}$ existed when its temperature was raised to -50°C . This would correspond to a material having a saturated vapor pressure of about 2×10^{-8} torr if one assumes that the material has a molecular weight of about 300 g. After material from the cold finger had been allowed to sublime and deposit on the microbalance, the rate of sublimation at -21°C was $2 \times 10^{-8} \text{ g/cm}^2/\text{s}$ which corresponded to a vapor pressure of 3×10^{-7} for the same molecular weight assumption. This rate, however, was not constant but decreased rapidly after the initial rate. Subsequent warming to -1°C resulted in a sublimation at about the same rate experienced at -21°C . A return to a lower temperature of -12°C indicated a rate corresponding to a vapor pressure of 3×10^{-8} torr.

The fact that at -21°C the pressure is higher than at -12°C infers that at least two materials had condensed on the crystal. Also, the rapid drop in rate at -21°C indicated that one of the materials was sublimed during that period. A resume of the above experience is shown in Table 2.

Table 2
The Behavior of Materials A and B

| Test Sequence | Temperature (°C) | Material A | | Material B | |
|---------------|------------------|---|--------------------------|--------------------|--------------------|
| | | ϕ (g/cm ⁻² · s ⁻¹) | P _s (torr) | ϕ | P _s |
| 1 | -50 | 1×10^{-9} | 2×10^{-8} | | |
| 2 | -21 | 2×10^{-8} | 3×10^{-7} | | |
| 3 | - 1 | | | 2×10^{-8} | 3×10^{-7} |
| 4 | -12 | | | 1×10^{-9} | 3×10^{-8} |

COMPARISON OF BLANKET AND CHAMBER DEGASSING

A comparison of the empty chamber and blanket weight losses and rates of weight losses are shown in Table 3.

Table 3
Comparison of Blanket and Chamber Degassing

| | Blanket | | Empty Chamber | |
|------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| | Total | L. V. Press. Mat. | Total | L. V. Press. Mat. |
| Total Wt. Losses | From Fig 1 | From Fig 2 | From Fig 1 | From Fig 2 |
| After 24 hr | 7.61×10^{-2} g | 7.76×10^{-3} g | 6.84×10^{-2} g | 1.68×10^{-3} g |
| After 60 hr | 1.06×10^{-1} g | 1.03×10^{-2} g | — | — |
| Rates of Weight Losses | From Fig 4 | From Fig 4 | From Fig 3 | From Fig 3 |
| After 1 hr | 3.8×10^{-6} g/s | 3×10^{-7} g/s | 4.2×10^{-6} g/s | 5.4×10^{-8} g/s |
| After 24 hr | 2.7×10^{-7} g/s | 2.5×10^{-8} g/s | 1.6×10^{-7} g/s | 7.5×10^{-9} g/s |
| After 40 hr | 2.5×10^{-7} g/s | 1.8×10^{-8} g/s | — | — |

Table 3 shows that the total weight losses of the blanket and the empty chamber were of the same order of magnitude after 24 hours of pumping. The rates of total weight losses were also about the same during the first 24 hours of pumping. After that period, the blanket total outgassing rate remained constant. The rates of the low vapor pressure materials were an order of magnitude lower for the empty

chamber than those of the blanket during the 24 hours in which comparison is possible. The fact that the total outgassing was of the same order of magnitude suggests that the outgassing in both cases was mostly from surface desorption and that the loss of heavy materials does not appreciably change the total outgassing values.

In regard to the nature of the outgassing, the slope of the total outgassing rate of the chamber shows it to be produced by surface desorption of several different molecules. On the other hand, the heavy molecular weight material was produced by a diffusion process during the initial 6 or 7 hours followed by a process resembling surface desorption. The outgassing from the blanket appeared to be a combination of surface desorption and diffusion during most of the time during which outgassing rates decayed. The constant rate shown to occur after 35 to 40 hours may be the result of sublimation of some material. The heavy material degassing resembled an initial diffusion process followed by surface desorption after six or seven hours. Its rate became constant after 40 to 45 hours. Other data from the chamber degassing were: (1) the outgassing rate decreased from 4×10^{-6} g/s to 4×10^{-7} g/s in 10 hours and it would decay another order of magnitude after approximately 100 hours and (2) the low vapor pressure material outgassing rate decayed from 5.5×10^{-8} g/s to 5.5×10^{-9} g/s in approximately 30 to 35 hours. These rates are based on a 60°C wall temperature. At other temperatures, longer or shorter times would be needed to accomplish the same outgassing. Estimates of required times have been indicated previously. The outgassed material was mostly water with traces of phthalates and hydrocarbons. Of course, traces of other materials will be found in these tests, depending on the previous history and uses of the chamber.

CONCLUSIONS AND SUMMARY

Crystal microbalances can be employed to provide accurate measurements of evaporation and sublimation phenomena in a vacuum chamber. They can also provide, by appropriate variations of their temperatures, a means of identifying materials with different saturated vapor pressures.

The described test on the outgassing at 60°C of an ERTS blanket has indicated that

- The blanket lost about 1×10^{-1} g of material in 60 hours of vacuum exposure. Of this amount, about one-tenth consisted of heavy molecular weight materials with vapor pressures varying from 2×10^{-8} torr at -50°C to 3×10^{-7} torr at -1°C .

- The rate of outgassing after 45 hours was about 2.5×10^{-7} g/s and appeared to remain constant.
- Gas chromatography/mass spectrometry and infrared radiometry indicated that in addition to ambient gases, the outgassing included traces of hydrocarbon oxides, phthalates, and tetrabutoxyethylene. Hydrocarbon oxides are frequently found when organic materials are present. The origin of phthalates cannot be defined but are often found in tests of spacecraft hardware. The tetrabutoxyethylene probably originated from a flow agent used in D-4D blanket paint.

On the accretion of the above outgassing on a -10°C surface, the microbalance showed that

- Accumulation occurred on this surface at a rate of 1×10^{-10} g/cm² · s for 2 or 3 hours. This rate decayed to about 1×10^{-11} g/cm² · s after 35 hours and continued to diminish very slowly.
- The total accretion was 7.5×10^{-6} g/cm² in 60 hours.
- The materials accreted appear to be deposits of a combination of materials having vapor pressures from 1×10^{-8} to 10^{-7} torr in the range of temperatures -50 to -1°C .

The following are comments on the blanket outgassing and its deposition on critical surfaces.

- In about 40 hours the accelerated test at 60°C accomplished the removal of surface adsorbed molecules and some sublimation of low and high molecular weight fractions of the blanket material.
- A portion of the surface desorbed molecules will be reacquired by the blanket when this is re-exposed to ambient conditions.

A portion of the diffusing and subliming molecules of the blanket has been removed by this test. The return of the blanket to a vacuum environment would resume the outgassing of subliming materials, and the desorption of surface reacquired molecules. The venting of gas trapped between mylar layers will also reoccur. The rate of material

sublimation will be a function of the material temperature.

The time to reach steady-state outgassing at +20° C will be almost double the time noted here.

For a spacecraft in orbit, at about ambient temperature, bulk accretion of blanket outgassing on a critical surface at -4° C will probably not occur for the following reasons.

- The rate of sublimation in space will be smaller than in this test because the material will be at a temperature less than +60° C. A larger dispersion of the contaminant will exist (the chamber simulates the dispersion at about 2- to 300-km altitude) while the spacecraft orbits at about 900 km. As a result of this, the flux required for accretion on the -4° C surface will not be available. However, accretion could occur if the surface is directly exposed to or is in the path of such a flux.

Some of the results of the outgassing of this particular chamber at +60° C are the following.

- The initial outgassing rate was 4×10^{-6} g/s. It is reduced to 4×10^{-7} g/s in about 10 hours, and it appears that another order of magnitude drop would be obtained in about 100 hours.
- The outgassing is of surface origin, and most of it can be removed in 24 hours at this temperature.
- The portion of the outgassing consisting of heavy molecular weight materials had an initial rate of 5×10^{-8} g/s. It comes off at a high rate during the first 7 or 8 hours of degassing and becomes less than 1×10^{-8} after 18 hours.
- It is estimated that the above events would occur in about double the indicated time at an outgassing temperature of +20° C but 30 percent less time for an outgassing at +100° C.

As expected, phthalates and hydrocarbons were components of the outgassing. The quantities of these components and others are predicated on the previous history of the chamber.

REFERENCES

1. K. H. Behrndt. "Long Term Operations of Crystal Oscillators in Thin Film Deposition." *Journal of Vacuum Science and Technology*. 8. No. 5. Sept - Oct 1971. pp. 622-626
2. A. E. Barrington. *High Vacuum Engineering*. Prentice-Hall Inc. 1963. p. 55
3. P. A. Redhead, J. P. Hobson, and E. V. Kornelsen. *The Physical Basis of Ultrahigh Vacuum*. Chapman and Hall Ltd. London. 1968. p. 104
4. D. J. Santeler, D. H. Holkeboer, D. W. Jones, and F. Pagano. "Vacuum Technology and Space Simulation." NASA-SP-105. 1966. p. 186

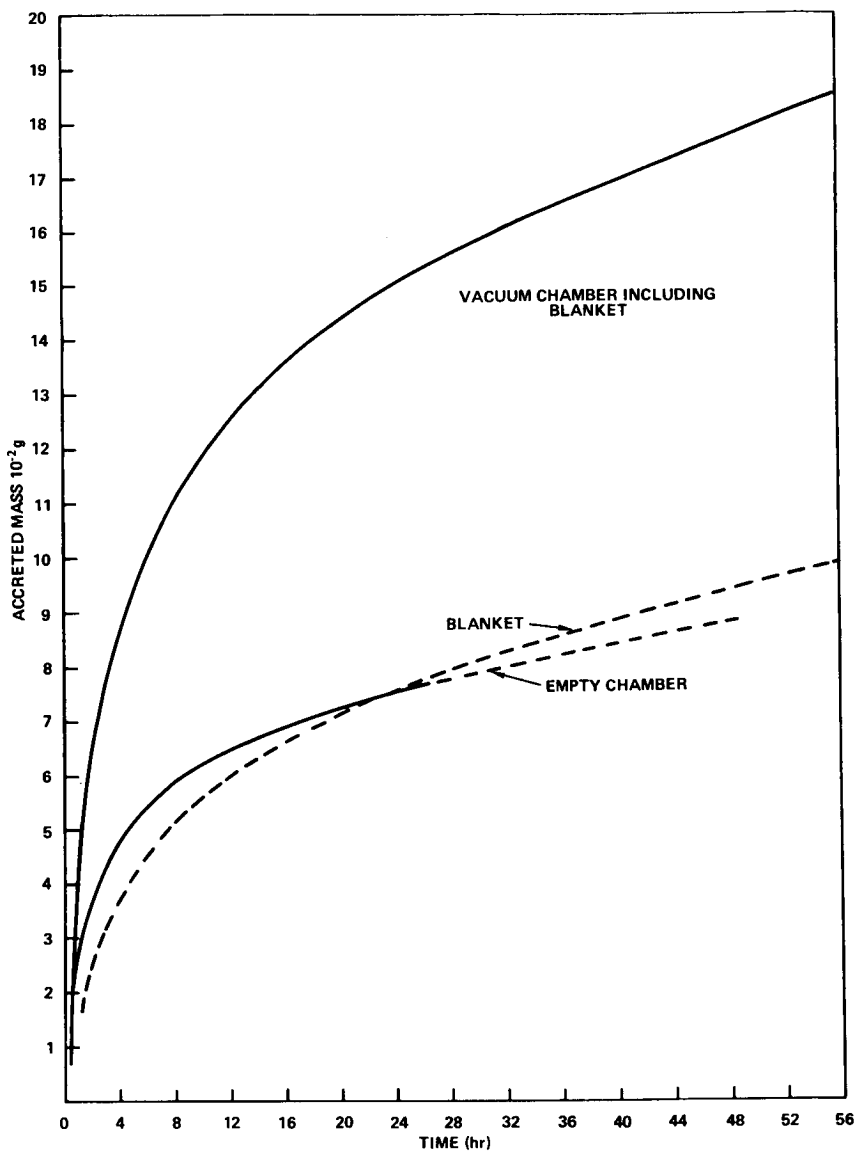


Figure 1. Total outgassing material accreted on -120°C surface.

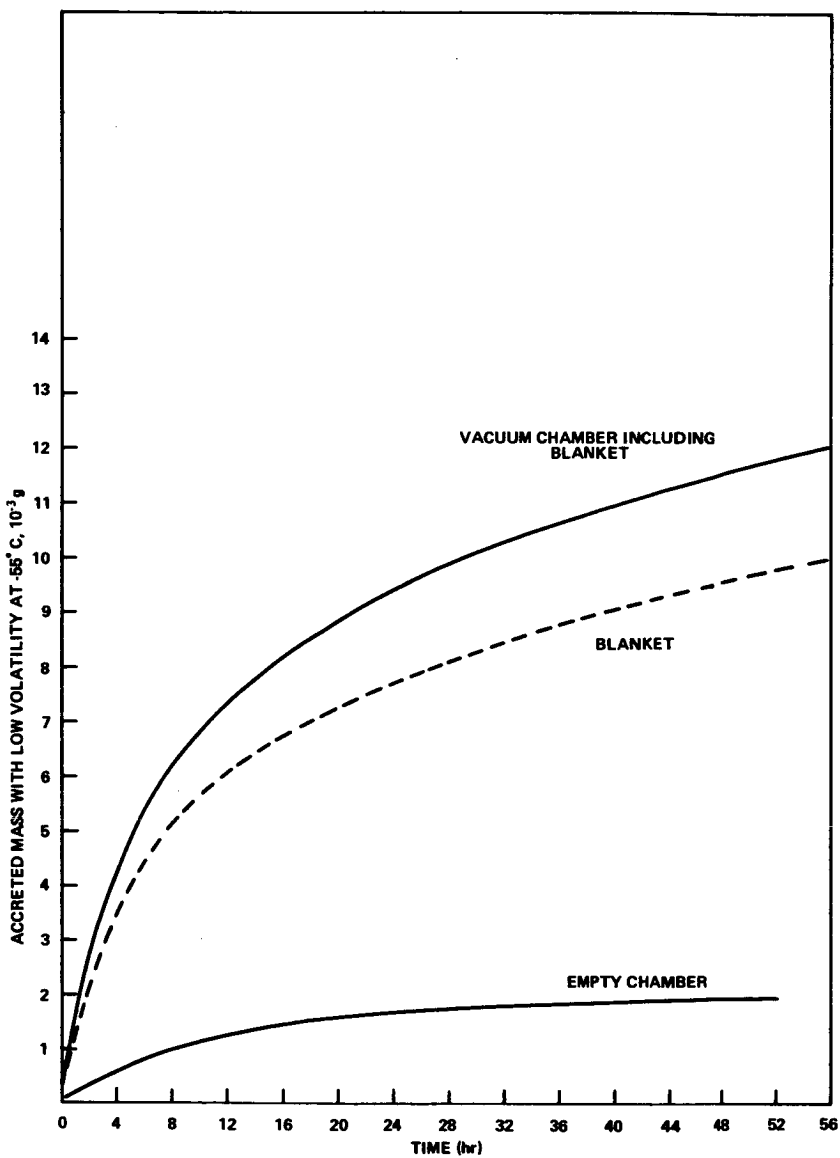


Figure 2. Accreted outgassing with low volatility at -55°C.

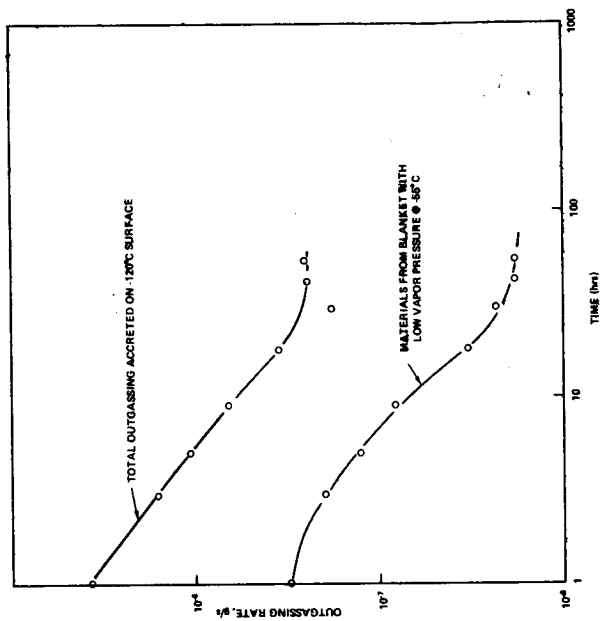


Figure 4. Outgassing rate of blanket at 60° C.

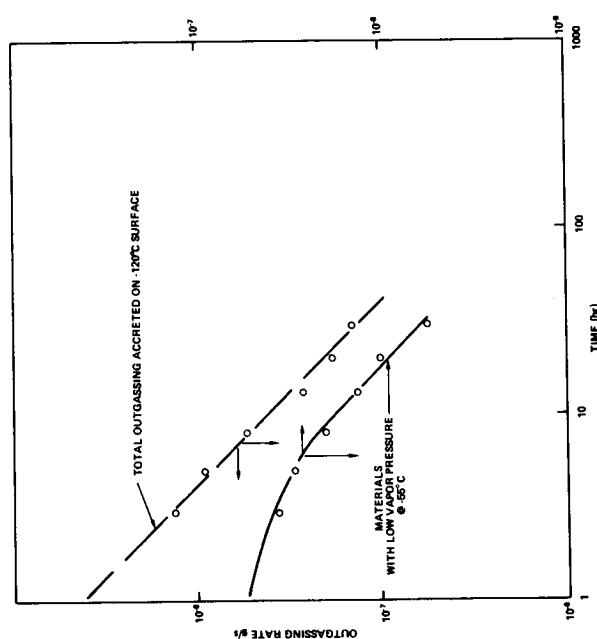


Figure 3. Outgassing rate of 3- by 3-ft chamber No. 240 at 60° C.

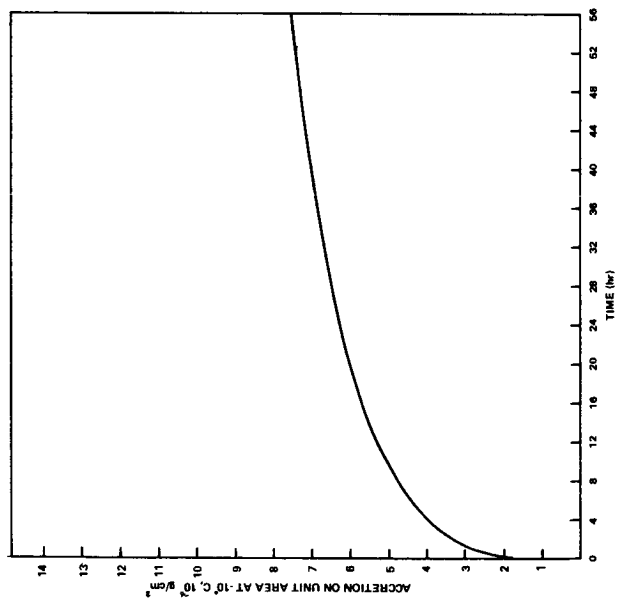


Figure 5. Blanket outgassing accreted on unit area at -10°C .

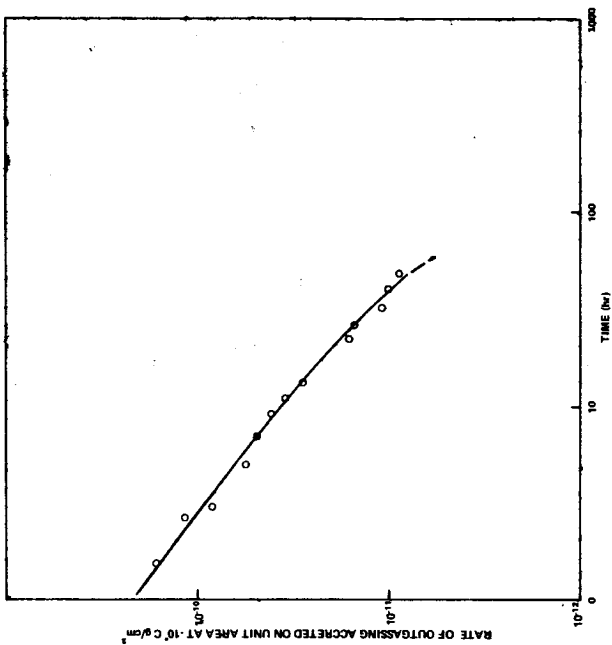


Figure 6. Rate of blanket outgassing accreted on unit area at -10°C .

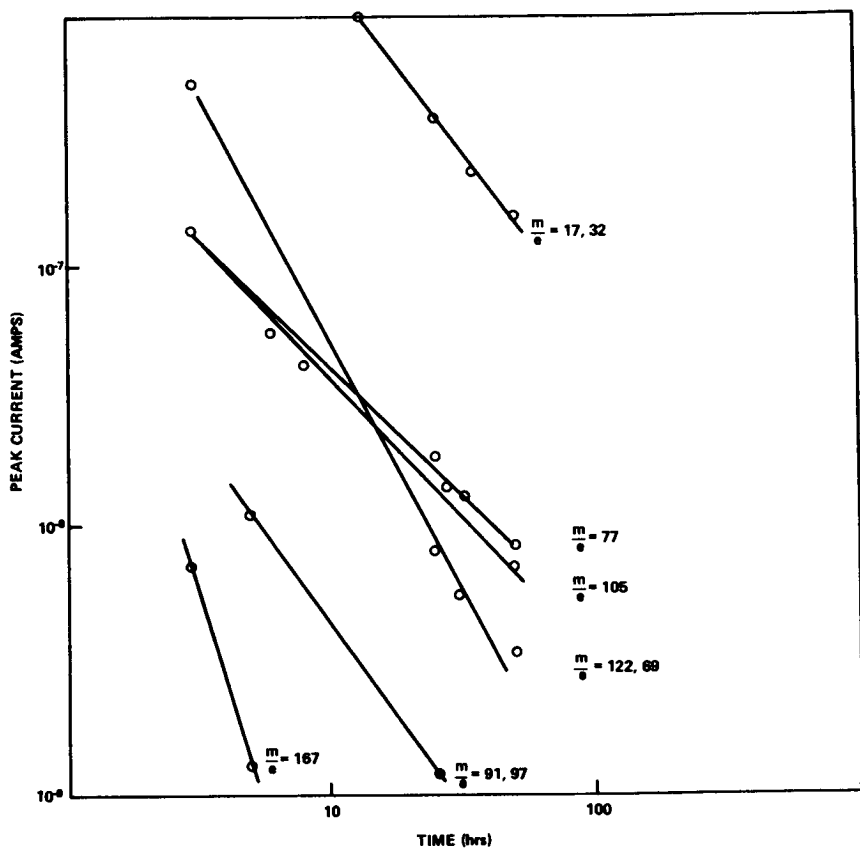


Figure 7. Sample mass spectrometer peak current readings.